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ONE POT SYNTHESIS OF ACETYLATED HOMOALLYL ALCOHOLS

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Abstract : An efficient one pot procedure for the preparation of acetylated homoallyl alcohols mediated by $TaCl_5$ is described.

Sakurai reaction[1] has become a most versatile tool to prepare homoallyl alcohols starting from allylsilanes and aldehyde wherein a new C-C bond is also created. This reaction is generally mediated by Lewis acids. Various mediators have been reported in literature to-date which include BF_3. OEt_2, $NbCl_5$, InI_3, $Sc(OTf)_3$, besides others.[2] The recent additions include chiral ligand assisted reactions[3] wherein good ee's of homoallyl alcohols are obtained. In a long synthetic scheme it may be desirable to protect the newly generated free alcohol before proceeding further. It would be more advantageous if both allylation and acetylation reactions are achieved in one pot. Thus, as part of a programme initiated at development and utilisation of $TaCl_5$ as Lewis acid,[4] we were interested in developing a new procedure for Sakurai reaction and insitu acetylation, the results of which are being presented herein (equation 1).

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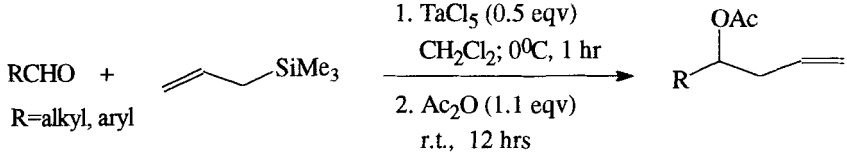
equation 1:

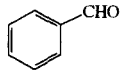
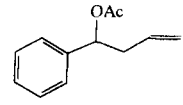
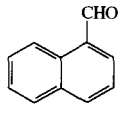
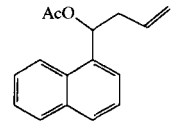
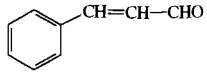
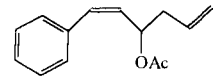
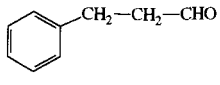
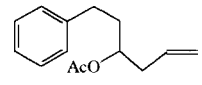
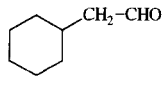
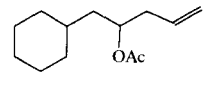
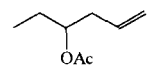
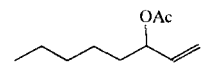
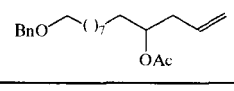


Initially benzaldehyde (entry 1, table 1) was treated with 0.5 eq. of tantalum chloride and 1.1 eq of allyltrimethylsilane in dry CH_2Cl_2 at 0°C for 1 hour (monitered by TLC) followed by addition of 1.1 eq of acetic anhydride yielded the corresponding acetylated homoallyl alcohol in 70% isolated yield. Also, naphthaldehyde (entry 2, Table 1) responded well to the reaction protocol and good yield of acetylated alcohol was obtained. In the case of conjugated aldehyde (entry 3, Table 1) no traces of 1,4-product was observed. Few other aliphatic aldehydes (entries 5,6,7 & 8, Table 1) also were consistent to the reaction conditions which explains the mildness of the procedure.

TYPICAL PROCEDURE :

To a stirred solution of 0.5 mmol of $TaCl_5$ (0.179 g) in 20 mL of dry CH_2Cl_2, which was cooled to 0°C was added 1.0 mmol of benzaldehyde (0.106 g) in dry CH_2Cl_2 under N_2 atmosphere. After stirring for 20 minutes 1.1 mmol of allyltrimethylsilane (0.125 g) in dry CH_2Cl_2 was added dropwise and allowed to stir at 0°C for 1 hour. Freshly distilled 1.1 mmol of Ac_2O (0.112 g) was added dropwise at 0°C and allowed to stir at room temperature for 12 hours. The total reaction mixture was quenched with a saturated solution of $NaHCO_3$ and stirred for 10 minutes. The reaction mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulphate, filtered and concentrated to give crude product (R_f=0.5, 5% ethyl acetate in hexane as eluting mixture). The crude product was purified by column chromatography over SiO_2 using hexane : ethylacetate (50 : 1) as eluting mixture, providing 0.114 g (70%) of acetylated homoallyl alcohol.

Table 1 :

Entry	Aldehyde		Product		Yield%*
1		1a		1b	70
2		2a		2b	66.7
3		3a		3b	70.5
4		4a		4b	50 4**
5		5a		5b	60
6	CH_3CH_2-CHO	6a		6b	55
7	$CH_3(CH_2)_5$-CHO	7a		7b	66
8	$BnO(CH_2)_9$-CHO	8a		8b	57

* Yields based on isolation of chromatographically homogenous products

** About 15% of alcohol was also isolated

Analytical and spectroscopic data of compounds :

1b: IR (neat) : 845cm^{-1}, 1737cm^{-1} . ^{1}H NMR($CDCl_3$) : δ 7.21-7.51 (m, 5H), 5.67 (t, 1H, J=7.01 Hz), 5.62-5.71 (m, 1H), 5.15-5.21 (m, 2H), 2.45-2.51 (m, 2H), 2.05 (s, 3H) ; MS (M^+) : 190; Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.41; found : C, 75.36; H, 7.28.

2b: IR (neat) : 848cm^{-1}, 1734cm^{-1} . ^{1}H NMR($CDCl_3$) : δ 7.41-8.21 (m, 7H), 6.65(t, 1H, J=5 Hz), 5.72-5.92 (m, 1H), 5.15-5.23 (m, 2H), 2.80 (t, 2H, J=7.5 Hz), 2.15 (s, 3H); MS (M^+) : 240; Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.98; H, 6.70; found : C, 79.38; H, 6.25.

3b: IR (neat) : 848cm^{-1}, 1736cm^{-1} . ^{1}H NMR($CDCl_3$) : δ 7.21-7.45 (m, 5H), 6.60(d, 1H, J=15.5 Hz), 6.15 (dd, 1H, J=15.5 Hz), 5.60-5.80 (m, 1H), 5.15-5.62 (m, 2H), 2.50 (t, 1H, J=6 Hz), 2.05 (s, 3H); MS (M^+) : 216; Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.45; found : C, 77.25; H, 7.38.

4b: IR (neat) : 849cm^{-1}, 1735cm^{-1} . ^{1}H NMR($CDCl_3$) : δ 6.95-7.22 (m, 5H), 5.51-5.72 (m, 1H), 4.91-5.08 (m, 2H), 4.75-4.85 (m, 1H), 2.45-2.62 (m, 2H), 2.15 (t, 2H, J=7 Hz), 2.01 (s, 3H); 1.82-1.95 (m, 2H) MS (M^+): 218; Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31; found : C, 76.97; H, 8.25.

5b: IR (neat) : 848cm^{-1}, 1735cm^{-1} . ^{1}H NMR($CDCl_3$) : δ 5.60-5.80 (m, 1H), 4.95-5.12 (m, 2H), 4.12-4.55 (m, 1H), 2.25-2.35 (m, 2H), 2.05 (s, 3H), 0.81-1.82 (m, 13H); MS (M^+) : 210; Anal. Calcd. for $C_{13}H_{22}O_2$: C, 74.25; H, 10.55; found : C, 74.01; H, 10.23.

6b: IR (neat) : 848cm^{-1}, 1735cm^{-1} . ^{1}H NMR($CDCl_3$) : δ 5.65-5.75 (m, 1H), 5.05-5.15 (m, 2H), 4.82-4.91 (m, 1H), 2.35-2.45 (m, 2H), 0.85-1.00 (m, 5H), 2.08 (s, 3H), 0.81-1.00 (m, 5H); MS (M^+) : 142; Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.92; found : C, 67.25; H, 9.61.

7b: IR (neat) : 847cm^{-1}, 1735cm^{-1} . ^{1}H NMR($CDCl_3$) : δ 5.62-5.75 (m, 1H), 5.12-5.15

(m, 2H), 4.85-4.95 (m, 1H), 2.25-2.45 (m, 2H), 2.01 (s, 3H), 0.82-1.15 (m, 13H); MS (M^+) : 180; Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 12.21; found : C, 73.15; H, 12.01.

8b: IR (neat) : 846cm^{-1}, 1737cm^{-1} . ^{1}H NMR($CDCl_3$) : δ 7.21-7.35 (m, 5H), 5.66-5.82 (m, 1H), 5.01-5.15 (m, 2H), 4.85-4.95 (m, 1H), 4.49 (s, 2H), 3.35 (t, 2H, J=5.88 Hz), 2.30-2.35 (m, 2H), 2.01 (s, 3H), 1.12-1.75 (m, 16H); MS (M^+) : 346; Anal. Calcd. for $C_{22}H_{34}O_3$: C, 76.26; H, 9.88; found : C, 76.14; H, 9.58.

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